Sr2(Nd, Ce)2MCu2O9, M=Al, Co, Ga. A new layered copper oxide structure type

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$Sr_2(Nd, Ce)_2MCu_2O_9$, M=Al, Co, Ga

A new layered copper oxide structure type

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A new layered copper oxide structure type is reported based on the ordered interleaving of AlO_4, CoO_4 or GaO_4 tetrahedra between the apices of copper oxide pyramids, and an $(Nd, Ce)_2O_2$ fluorite layer between the bases of the pyramids. Despite the structural similarities to the recently reported $Sr_2(Y, Ca)GaCu_2O_7$ and $Sr_2(Nd, Ce)_2NbCu_2O_{10}$ superconducting structure types, we have not been able to find conditions which produce superconductivity in the present materials.

1. Introduction

The known copper oxide based superconductors are derived from the structural interleaving of CuO_2 planes with a variety of metal–oxygen layers. These layers act as separators and frequently also as the part of the structure which is chemically manipulated to induce the optimal hole concentration in the CuO_2 planes. Many classification schemes have been proposed in recent years to help clarify the known structures and predict the existence of possible new ones. Based on the recent successes [1–3] in finding superconductivity in compounds with new kinds of intermediary layers ($Sr_2LnGaCu_2O_7$, and $Sr_2Ln_2NbCu_2O_{10}$, Ln=Lanthanide) we have attempted to synthesize, and induce superconductivity in, a new structure type which is a hybrid of these two, of the general formula $Sr_2Ln_2MCu_2O_9$. M is an atom tetrahedrally coordinated to oxygen, e.g. Ga, Co, or Al, each of which has been found to yield a 123 related structure $Sr_2LnMCu_2O_7$ with layers of MO_4 tetrahedra [4–7]. We have in fact succeeded in synthesizing the new structure type, but have been unable to find synthetic conditions to make it superconducting.

Our model for the crystal structure of $Sr_2(Nd, Ce)_2GaCu_2O_9$ is shown in fig. 1. The same structure, the only difference being the degree of ordering for the orientations of the MO_4 tetrahedra, occurs for the Al and Co analogs. The new structure type is shown between the two related structures from which it is derived, $Sr_2LnGaCu_2O_7$ and $Sr_2Ln_2NbCu_2O_{10}$. Its very close relation to the latter structure type is clearly seen in the figure, with the replacement of the plane of NbO_6 octahedra by a plane of GaO_4 tetrahedra. The plane of GaO_4 tetrahedra is analogous to that shown for $Sr_2LnGaCu_2O_7$.

Starting materials for synthesis were $SrCO_3$, dried Nd_2O_3, $Ce_2(CO_3)_3{\cdot}5H_2O$, Ga_2O_3, $Al(NO_3)_3{\cdot}9H_2O$, CoC_2O_4 and CuO. They were mixed in the appropriate ratio to yield $Sr_2Nd_{2-x}Ce_xMCu_2O_{9\pm\delta}$ for M=Al, Co, Ga and x=0.35, 0.5 and 0.65, to span the composition region expected to be optimal for superconductivity. All materials were initially slowly heated to 1000°C in O_2 and held there several days with intermediate mechanical grindings. The final synthetic conditions yielding the best phase purity were found to be different for each of the different tetrahedral ions.

2. Ga compounds

For the Ga based compounds,

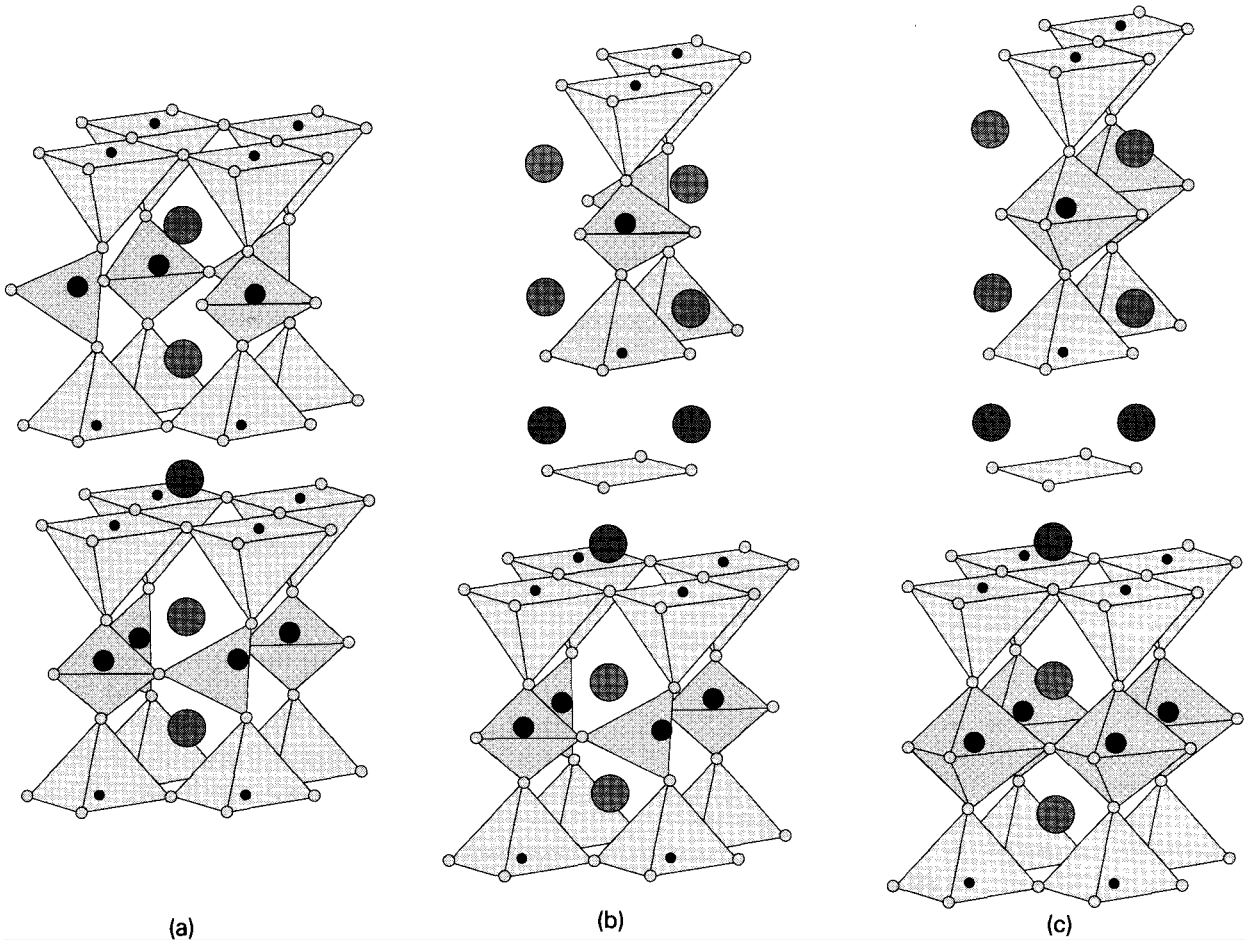

Fig. 1. Comparison of the new $Sr_2(Nd, Ce)_2GaCu_2O_9$ structure type (b) with $Sr_2NdGaCu_2O_7$ (a) and $Sr_2(Nd, Ce)_2NbCu_2O_{10}$ (c). Open circles, oxygen; small dots, copper; large shaded circles, rare earths and alkaline earths; medium dark circles, Ga or Nb.

$Sr_2Nd_{2-x}Ce_xGaCu_2O_9$, relatively high temperatures were necessary for synthesis, but good phase purity was obtained. After the initial 1000°C treatments, samples were heated successively at 1050, 1125 and 1150°C for 2 days at each temperature in O_2 with intermediate grindings. Single phase material was obtained for x=0.65; impurities were estimated to be on the order of 5% (by powder X-ray diffraction) for the other compositions. The samples were not superconducting. In analogy to the processing for $Sr_2Nd_{1.5}Ce_{0.5}NbCu_2O_{10}$, the samples were then heated for 3 days at 25 atm O_2 pressure at 1150°C and then cooled in 100°C steps, with 5 h soaks, to 550°C, and finally furnace cooled to ambient temperature. The phase purity was not significantly changed, and the samples did not become superconducting.

The powder X-ray diffraction pattern was indexed by analogy to the unit cells of $Sr_2LnGaCu_2O_7$ [4,5] and $Sr_2Ln_2NbCu_2O_{10}$ [8,9]. The c-axis is very similar in length to that of the Nb containing compounds, but the symmetry is strongly distorted from tetragonal, as is observed for the 123 related Ga containing compounds, due to the presence of chains of GaO_4 tetrahedra running in the basal plane parallel to the simple perovskite 110 direction. The refined crystallographic cell is C centered orthorhombic, with a=5.456, b=5.529 and c=28.34 Å. The powder dif-

fraction pattern in tabular form is presented in table 1.

Determination of the absolute oxygen content of $Sr_2Nd_{1.35}Ce_{0.65}GaCu_2O_{9-\delta}$ is complicated by the fact that CeO_2 is only partially reducable (not to a stoichiometric oxide) on heating in the TGA to 1000°C in 5% H_2 95% N_2, our standard method for oxygen content determination. Finely powdered material can be reduced in such a gas mixture at 500°C, a temperature where CeO_2 will not lose oxygen on heating. Reduction of the material prepared at 1150°C at 25 atm O_2 pressure and step cooled yielded a value of δ=0.25, indicating that no oxidation of copper had occurred even in the 25 atm O_2 anneal.

Table 1
Powder X-ray diffraction of $Sr_2(Nd, Ce)_2GaCu_2O_9$ (Cu Kα), a=5.4560(7) Å, b=5.5289(5) Å and c=28.340(3) Å

Index	$2\theta_{obs}$	$2\theta_{calc}$	I/I_0
002	6.214	6.232	5
111	23.079	23.096	4
113	24.753	24.765	13
008	25.099	25.116	1
115	27.812	27.823	7
0010	31.550	31.541	7
117	31.899	31.904	100
020	32.340	32.256	29
200	32.820	32.800	43
119	36.700	36.711	2
028	41.398	41.393	5
208	41.761	41.753	5
1111	42.040	42.049	8
0014	44.717	44.729	13
0210	45.810	45.813	8
2010	46.144	46.145	8
220	46.751	46.740	41
222	47.203	47.203	2
133	53.316	53.308	1
313	53.888	53.901	4
0214	56.291	56.277	7
2014	56.564	56.564	7
137	57.428	57.424	18
317	57.996	57.989	19
0018	58.601	58.578	4
1117	60.367	60.372	9
1311	64.405	64.402	2
3111	64.932	64.931	2
0020	65.841	65.854	8
040	76.728	67.730	2
0218	68.530	68.526	1
2018	68.794	68.783	5
1315	73.835	73.835	1
3115	74.330	74.332	3
240	77.316	77.318	7
2218	78.063	78.074	6
1317	79.403	79.405	2

Thin specimens for electron microscopy were obtained by crushing. Electron microscopy was performed with a Phillips CM30ST electron microscope operating at 300 kV and equipped with side-entry 25°/25° tilt specimen holder and a Link EDX element analysis system.

The high resolution electron microscope (HREM) images were recorded at a series of defocus values, and in particularly a defocus of about –40 nm at which all cations in [110] images are imaged as dark dots, or at a defocus of about –80 nm where the cations are imaged as bright dots in [110] images. Image calculations were carried out using a MacTempas software program, in which the following parameters were used: Cs is 1.2 mm, defocus spread is 9 nm, objective aperture is 6.5 nm^{-1}, beam convergence is 1.2 mrad, and mechanical vibration is 0.05 nm. The thickness and defocus were varied.

A number of experimental HREM images were averaged over a number of unit cells to improve the ability to measure gray values of the various positions. For this purpose a TCL image processing software package was used. Images were digitized with about 50 pixels per nm. These images were noise reduced by first averaging each pixel over itself and its eight neighbours and next by averaging the image over a number of unit cells.

Electron diffraction was carried out with a number of crystals, which were rotated to scan the reciprocal space. Electron diffraction patterns of the [001], [010] and [011] orientations are given in fig. 2. The diffraction patterns indicate an orthorhombic $a_p\sqrt{2}$, $a_p\sqrt{2}$, c unit cell with a=5.46, b=5.53 and c=28.3 Å. The systematic absences of the reflections indicate the space group to be $Cmc2_1$.

HREM was performed to determine the structure of $Sr_2(Nd, Ce)_2GaCu_2O_9$. The observed [011] images reveal the stacking of the various layers because all cations can be imaged as individual dark dots. An example is given in fig. 3(c). The [010] and [001] images (see fig. 3(a) and (b)) can give information on deviations from a simple a_p, a_p, c structure. Image calculations have been carried out with a model based on the structure of $Sr_2NdGaCu_2O_7$ [4], in which one O_2 layer and a Nd layer have been added with a sub-

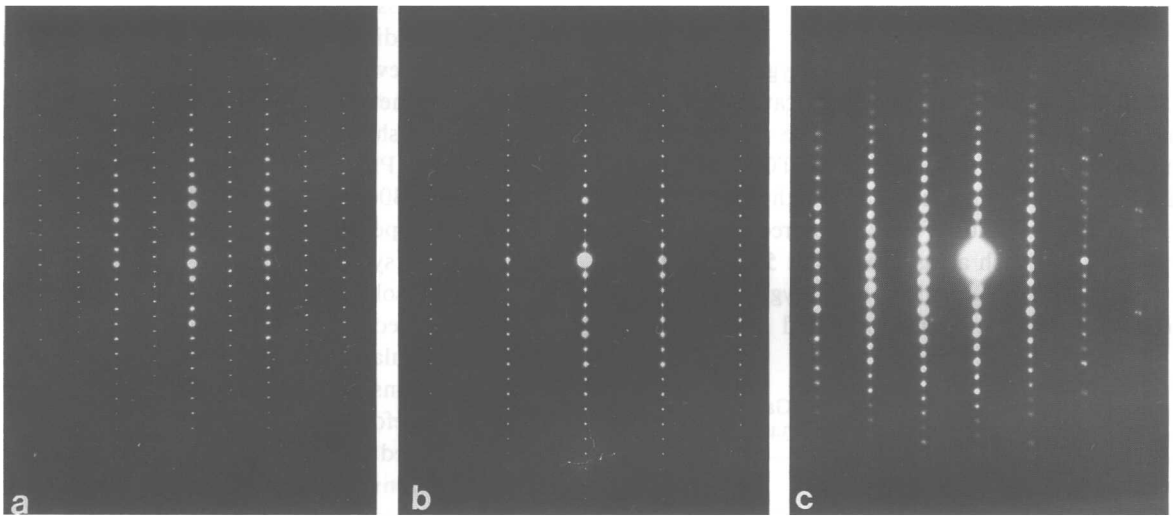

Fig. 2. Electron diffraction patterns of $Sr_2Nd_{1.35}Ce_{0.65}GaCu_2O_{9-\delta}$ along (a) [001], (b) [010] and (c) [011].

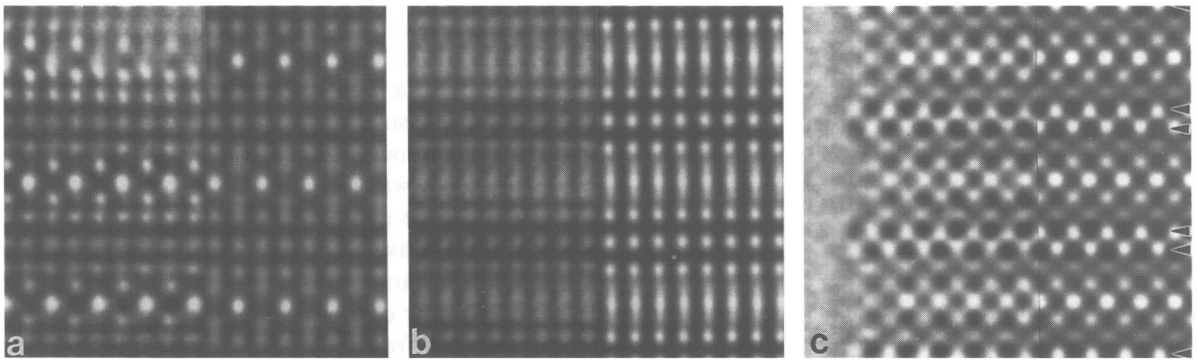

Fig. 3. Averaged experimental HREM images of $Sr_2(Nd, Ce)_2GaCu_2O_{9-\delta}$ taken along (a) [001], (b) [010] and (c) [011]. The images were obtained by averaging over 8, 4 and 8 unit cells, respectively. Insets show the calculated images for a thickness of 2 nm and a defocus of –40 nm.

sequent increase in the *c*-axis of 0.275 nm. The calculated images, given as insets in the figs. 3(a), (b) and (c) show a good agreement with the experimental images.

The temperature dependence of the resistivity of a $Sr_2Nd_{1.35}Ce_{0.65}GaCu_2O_9$ polycrystalline pellet is shown in fig. 4. The measurement was DC, with a four-probe bar geometry. The sample is very poorly conducting, with a room temperature resistivity of approximately 100 m Ω cm. The plot of log resistivity versus $(1/T)^{1/2}$ suggests transport by variable range hopping.

3. Co compounds

For the Co analog, samples of $Sr_2Nd_{2-x}Ce_xCoCu_2O_9$ in the composition range $0.35 \leq x \leq 0.65$ were multiple phase under all synthetic conditions attempted. Often 123-like $Sr_2NdCoCu_2O_7$ was a major impurity phase. Considerably better phase purity was obtained for materials prepared at higher Ce contents (copper valences closer to 2+). For $Sr_2Nd_{1.2}Ce_{0.8}CoCu_2O_9$ prepared at a final temperature of 1050°C in O_2 (60 h) the powder X-ray diffraction pattern was well indexed on a body centered tetragonal unit cell, with

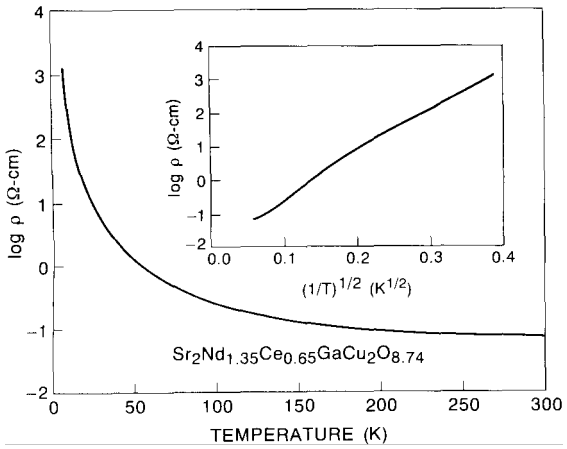

Fig. 4. Temperature dependent resistivity of $Sr_2Nd_{1.35}Ce_{0.65}GaCu_2O_{9-\delta}$.

refined cell parameters a=3.869, c=28.33 Å. Electron diffraction revealed the true cell in the basal plane to be $a_p\sqrt{2}\times a_p\sqrt{2}$, for a true a=5.471. The true symmetry on a local scale may in fact be slightly orthorhombic, with $a\neq b$. Three impurity peaks ranging in relative intensity in 4–8% of the strongest major phase peak were observed below 50°2θ (Cu Kα radiation) suggesting that slightly different synthetic conditions or compositions would be necessary to produce perfect single phase material. When tested (magnetically, AC susceptibility) at 4.2 K, none of the samples of the Co based material showed any sign of superconductivity. In analogy to $Sr_2YCoCu_2O_7$ [6], the Co tetrahedra in this new phase are also likely to be aligned along the 110 direction. Unlike the Ga case however, where the 110 GaO_4 chains are long range ordered, for both the Co and Al [7] analogs the MO_4 tetrahedral chains are only short range ordered, yielding overall average tetragonal symmetry when averaged over the two possible 110 directions in the basal plane.

4. Al compounds

For the material with Al in the tetrahedral site, $Sr_2Nd_{1-x}Ce_xAlCu_2O_9$, single phase materials were obtained in one atmosphere of oxygen pressure only for x near 1 where the appropriate doping for superconductivity would not occur. The best results were obtained for $Sr_2Nd_{1.2}Ce_{0.8}AlCu_2O_{9\pm x}$ prepared at a final temperature of 1075°C (60 h) in O_2. All peaks in the powder X-ray pattern with intensities of 2% or greater of the most intense line could be indexed on the tetragonal I centered cell, with a=3.885 and c=27.93 Å. Again, electron diffraction showed the true basal plane repeat to be $a_p\sqrt{2}\times a_p\sqrt{2}$, with a true a=5.493. As for the Co analog, electron microscopy results suggest that the true local symmetry is orthorhombic, with disorder in the orientations of the AlO_4 tetrahedra chains giving rise to an overall average tetragonal symmetry. As there are two stacking sequences of atoms per c-axis repeat, the 0.4 Å smaller c, when compared to the Co analog, implies that the AlO_4 tetrahedra are 0.2 Å flatter or perhaps more distorted than are the CoO_4 tetrahedra.

Annealing of samples of composition $Sr_2Nd_{2-x}Ce_xAlCu_2O_{9-\delta}$ at 1050°C for 3 days at 30 atm ($0.8\leq x\leq 0.35$) also did not yield single phase materials for x<0.80. The samples were cooled in 100°C steps with 5 h soaks to a minimum temperature of 650°C before being cooled to room temperature in the furnace. We could find no indication for the presence of superconductivity on testing by AC magnetic susceptibility at 4.2 K.

Samples of $Sr_2Nd_{1.35}Ce_{0.65}GaCu_2O_{9-\delta}$ and $Sr_2Nd_{1.35}Ce_{0.65}AlCu_2O_{9-\delta}$ of the best phase purity from the 1 atm O_2 syntheses were treated at 180 atm O_2 to attempt to induce superconductivity. The treatment temperature was 950°C for a time of 50 h. Samples were cooled at 1°C/minute to 350°C and then furnace cooled to room temperature before removing from the furnace. The samples gained only very slightly in weight during the treatment, indicating that an insignificant amount of oxygen was absorbed at the high pressure. The samples were not superconducting at 4.2 K.

5. Conclusion

In conclusion, we have described and characterized a new layered copper oxide structure type based on the interleaving of double fluorite blocks between the bases of CuO_5 pyramids, and MO_4 tetrahedra between their apices. Despite the strong structural similarities between the new $Sr_2Nd_{2-x}Ce_xMCu_2O_9$ (M = Ga, Al, Co) structure type and those previ-

ously reported to be superconducting, $Sr_2(Ln,Ca)GaCu_2O_7$ and $Sr_2Nd_{2-x}Ce_xNbCu_2O_{10}$, we could not find the conditions which would successfully induce superconductivity. The problem is clearly related to the degree of hole doping attainable: in the Ga based materials, although the appropriate Nd/Ce ratios can be made, the compound is highly oxygen deficient; for the Co and Al based materials, even at O_2 pressures up to 30 atm, a maximum of only half the appropriate hole doping is obtained, as the proper Nd:Ce ratios cannot be made. It may be that synthesis under higher oxygen pressures and/or temperatures would lead to superconductivity in this structure type, through the attainment of the correct hole concentration.

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